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Title of the Invention: SOLID ELECTROLYTIC CAPACITOR

Abstract:

A solid electrolytic capacitor comprising:

a dielectric oxide coating formed on a metal on which a coating is to be formed;  
a first electrically conductive polymer film formed on the dielectric oxide coating, wherein the first electrically conductive polymer film is obtained by a chemical oxidation method with an oxidizing agent; and  
a second electrically conductive polymer film formed on the first electrically conductive polymer film, wherein the second electrically conductive polymer film is obtained by an electrolytic polymerization method; wherein  
said first and second electrically conductive polymer films constitute double layered electrically conductive polymer films which are used as a solid electrolyte.

## ⑫ 公開特許公報(A)

昭63-173313

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⑭ 発明の名称 固体電解コンデンサ

⑯ 特 願 昭62-4053

⑰ 出 願 昭62(1987)1月13日

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## 明 細 書

## 1. 発明の名称

固体電解コンデンサ

## 2. 特許請求の範囲

1. 皮膜形成金属に誘電体酸化皮膜を形成し、該誘電体酸化皮膜上に酸化剤を用いて化学酸化重合した導電性高分子膜を形成し、更に該導電性高分子膜上に電解重合により得られる導電性高分子膜を積層して、二重に形成された導電性高分子膜を固体電解質として用いることを特徴とする固体電解コンデンサ。

2. 皮膜形成金属がアルミニウムまたはタンタルである特許請求の範囲第1項記載の固体電解コンデンサ。

3. 酸化剤を用いて化学酸化重合した導電性高分子膜がポリピロールである特許請求の範囲第1項記載の固体電解コンデンサ

4. 電解重合により得られる導電性高分子膜がポリピロールである特許請求の範囲第1項記載の固体電解コンデンサ。

## 3. 発明の詳細な説明

(産業上の利用分野)

本発明は導電性高分子を固体電解質として用いたコンデンサに関する。

(従来技術)

近年デジタル機器の発展に伴ない、高周波領域においてインピーダンスの低い高周波特性の優れた大容量のコンデンサの出現が待たれ、この分野の研究が盛んになっている。現在知られている高周波特性の優れたコンデンサには、フィルム、マイカ、セラミックス等のコンデンサがあるが、1 $\mu$ F以上の静電容量を得ようとする、サイズが大きくなり、価格も非常に高くなる。

また大容量のコンデンサとして知られている電解コンデンサには電解液式と固体式とがある。前者の電解コンデンサは液状の電解質を用いているのでイオン伝導であるため、高周波領域において著しく抵抗が増大し、コンデンサのインピーダンスが増大する。後者の電解コンデンサには、固体電解質として、二酸化マンガンを使用するものと、

7,7,8,8-テトラシアノキノジメタン(TCNQと略す)錯体を使用するものがある。二酸化マンガンを固体電解質として用いたコンデンサにおいては、二酸化マンガ人が不溶の固体であるため、硝酸マンガンを熱分解して得られる二酸化マンガ人が固体電解質として用いられている。この熱分解は、通常数回繰り返して行なわれている。二酸化マンガ人は比抵抗が比較的高く、また繰り返して熱分解する際に誘電体である酸化皮膜を損傷しやすいなどの理由によりインピーダンスが高く、漏れ電流が大きいなどの欠点がある。TCNQ錯体を固体電解質として用いたコンデンサ(特開昭58-191414号、特開昭58-17609号など)では、TCNQ錯体は高い導電性を示すが、熱安定性に乏しいため、コンデンサ製造過程において分解し、絶縁体になることがあり、コンデンサの熱特性などに欠点がある。

まだ実用の域には達していないが電解重合による複素環式化合物の重合体を固体電解質としたコンデンサの製造法が提案された(特開昭60-

244017、特開昭61-2315など)。上記方法は、陽極酸化皮膜上に電解酸化により複素環式化合物のポリマー薄膜層を形成する方法である。この方法では、陽極酸化皮膜層が絶縁化されているので、電解酸化により陽極酸化皮膜層上に複素環式化合物を電解重合させることは不可能か、又は非常に困難である。また陽極酸化皮膜層のピンホールから電解酸化重合が起こったとしても不均一な膜となり、実用上大きな問題となる。

(発明が解決しようとする問題点)

導電性高分子の合成法は化学的酸化重合法および電解酸化重合法があるが、化学的酸化重合法では陽極酸化皮膜層上に強度の強い膜が形成できず、また電解酸化重合法では陽極酸化皮膜層が電気絶縁体であるため、電流を通さず、その上に強靱な導電性高分子膜を形成することができなかった。本発明の目的は電解重合法により得られた導電性高分子膜を固体電解質として使用し、静電容量が大きくかつ電気的特性、温度特性の優れた固体電解コンデンサを提供することにある。

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(問題点を解決するための手段)

本発明者らは上記問題点を解決するため種々検討した結果、皮膜形成金属に誘電体酸化皮膜を形成し、該誘電体酸化皮膜上に、酸化剤を用いて化学酸化重合した導電性高分子膜を形成し、更に該導電性高分子膜の上に、電解重合法により得られる導電性高分子膜を積層して、二重に形成された導電性高分子膜を固体電解質として用いることにより、静電容量の大きくかつ電気特性、温度特性の優れた固体電解コンデンサを提供することができた。

本発明を本発明の構成を示す第1図により更に詳しく説明すると、エッチングして表面を粗した皮膜形成金属(1)を電解酸化または空気酸化により該金属の酸化物を生成させ、誘電体酸化皮膜(2)を作成する。ついで誘電体酸化皮膜(2)上に、酸化剤を0.001mol/l~2mol/l含む溶液を塗布または噴霧などの方法により均一に分散した後導電性高分子の単量体を少なくとも0.01mol/l含む溶液または無溶媒で接触させるか、また

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は逆に導電性高分子の単量体を誘電体表面上に均一に分散した後酸化剤を接触させて、誘電体酸化皮膜層(2)上に化学酸化重合による導電性高分子膜(3)を形成し、表面を導電化する。ついで表面を導電化した皮膜形成金属を陽極とし、支持電解質を0.01mol/l~2mol/lおよび導電性高分子単量体を0.01mol/l~5mol/l含む電解液中にて電解酸化重合を行なうと、酸化剤を用いて重合した導電性高分子膜(3)の上に、電解酸化重合された強靱な導電性高分子膜(4)が得られる。更に一般的に用いられている銀ペーストなどにより封極リードを取り出し、エポキシ樹脂などにより外表すると本発明のコンデンサとなる。

本発明の皮膜形成金属はアルミニウムまたはタンタルを用いる。本発明の化学的酸化重合に用いられる酸化剤は、ヨウ素、臭素、ヨウ化臭素などのハロゲン、五フッ化ヒ素、五フッ化アンチモン、四フッ化ケイ素、五塩化リン、五フッ化リン、塩化アルミニウム、塩化モリブデンなどの金属ハロゲン化物、硫酸、硝酸、フルオロ硫酸、トリフル

オロメタン硫酸、クロロ硫酸などのプロトン酸、三酸化イオウ、二酸化窒素などの含酸素化合物、過硫酸ナトリウム、過硫酸カリウム、過硫酸アンモニウムなどの過硫酸塩、過酸化水素、過酢酸、ジフルオロスルホンルパーオキシドなどの過酸化物などの酸化剤を用いる。本発明の化学的酸化重合により形成される導電性高分子膜は、ポリピロール、ポリチオフェン、ポリアニリン、ポリフランを用い、特に好ましくはポリピロールを用いる。

本発明における支持電解質は陰イオンがヘキサフロロリン、ヘキサフロロヒ素、テトラフロロホウ素などのハロゲン化物アニオン、ヨウ素、臭素、塩素などのハロゲンアニオン、過塩素酸アニオン、アルキルベンゼンスルホン酸、ニトロベンゼンスルホン酸、アミノベンゼンスルホン酸、ベンゼンスルホン酸、 $\beta$ -ナフタレンスルホン酸等のスルホン酸アニオンであり、好ましくはスルホン酸アニオンである。また陽イオンがリチウム、ナトリウム、カリウムなどのアルカリ金属カチオン、ア

ンモニウム、テトラアルキルアンモニウムなどの四級アンモニウムカチオンである。化合物としては、 $\text{LiPF}_6$ 、 $\text{LiAsF}_6$ 、 $\text{LiClO}_4$ 、 $\text{NaI}$ 、 $\text{NaPF}_6$ 、 $\text{NaClO}_4$ 、 $\text{KI}$ 、 $\text{KPF}_6$ 、 $\text{KAsF}_6$ 、 $\text{KClO}_4$ 、 $\text{LiBF}_4$ 、トルエンスルホン酸ナトリウム、トルエンスルホン酸テトラブチルアンモニウムなどを掲げることができる。

本発明の電解酸化重合により得られる導電性高分子はポリピロール、ポリチオフェン、ポリアニリン、ポリフランを用い、好ましくはポリピロールを用いる。

以下実施例により本発明を具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

#### (実施例1)

電解酸化により化成処理を施して表面に酸化アルミニウム誘電体を形成させた厚さ $60\mu\text{m}$ のアルミニウム陽極箔を、過硫酸アンモニウム $0.04\text{mol/l}$ の水溶液に減圧下で10分間浸漬した後、乾燥した。これをピロール単量体 $2\text{mol/l}$ を含む

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アセトニトリル溶液に減圧下で10分間浸漬して、酸化アルミニウム誘電体上にポリピロール薄膜を化学酸化重合法により形成させた。ついで上記処理を行なったアルミニウム陽極箔をピロール単量体 $0.2\text{mol/l}$ 、シュウ酸 $0.02\text{mol/l}$ および支持電解質としてトルエンスルホン酸テトラブチルアンモニウム $0.05\text{mol/l}$ を含む水溶液中に浸漬した。該アルミニウム陽極箔を陽極とし、ステンレス板を陰極として電流密度 $0.5\text{mA/cm}^2$ の条件下で150分間定電流電解を行なった結果、均一な黒色のポリピロールの薄膜が表面に生成した。ついでこの表面に銀ペーストを用いて対極リードを取り出し、エポキシ樹脂により外装しコンデンサを完成させた。得られたコンデンサは120Hzにおいて静電容量 $2.2\mu\text{F/cm}^2$ で損失角の正接( $\tan\delta$ )は1.5%であった。なおこの箔の液中容量は $2.0\mu\text{F/cm}^2$ であるので110%の容量達成率であった。

#### (比較例1)

陽極箔上に化学酸化重合法によるポリピロール

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薄膜を形成せずに実施例1に準じて電解を行なったが、酸化アルミニウム誘電体上の一部にしかポリピロールが得られず、膜を形成することができなかった。

#### (実施例2)

ヨウ素 $0.1\text{mol/l}$ を含むエチルエーテル溶液を調整し、電解酸化により化成処理を施して表面に酸化アルミニウム誘電体皮膜を形成させた厚さ $60\mu\text{m}$ のアルミニウム陽極箔上に、先に調整したエチルエーテル溶液を噴霧して乾燥した。上記処理を行なったアルミニウム陽極箔をピロール単量体中に30分間減圧下で浸漬し、化学酸化重合法により黒色のポリピロール薄膜を形成した。以下実施例1に準じてコンデンサを完成した。得られたコンデンサは120Hzにおいて、静電容量 $2.0\mu\text{F/cm}^2$ 、 $\tan\delta$ は1.3%であった。

#### (実施例3)

電解酸化により化成処理を施して表面を酸化アルミニウム誘電体皮膜を形成させた厚さ $60\mu\text{m}$ のアルミニウム陽極箔を塩化第二鉄 $0.02\text{mol/l}$

1を含む水溶液に減圧下で2分間浸漬した後、乾燥した。これをピロール単量体0.1mol/lを含む水溶液に30分間浸漬し、化学酸化重合法により黒色のポリピロール薄膜を形成した。以下実施例1に準じてコンデンサを完成した。得られたコンデンサは120Hzにおいて、静電容量 $2.1\mu\text{F}/\text{cm}^2$ 、 $\tan\delta$ は1.8%であった。

#### (実施例4)

化成処理を施して表面に酸化タンタル誘電体皮膜を形成させたタンタル焼結体を過硫酸アンモニウム0.04mol/lの水溶液に減圧下で5分間浸漬した後、乾燥した。これをピロール単量体0.2mol/lおよびアジピン酸0.02mol/lを含む水溶液に減圧下で10分間浸漬して、酸化タンタル誘電体上にポリピロール薄膜を化学酸化重合法により形成させた。ついで上記処理を行なったタンタル焼結体をピロール単量体0.2mol/l、シュウ酸0.02mol/lおよび支持電解質として過塩素酸リチウム0.05mol/lを含む水溶液中に浸漬した。該タンタル焼結体を陽極とし、ステンレ

ス板を陰極として、電流密度 $0.5\text{mA}/\text{cm}^2$ の条件下で150分間、定電流電解を行なった結果、均一な黒色のポリピロールの薄膜が表面に生成した。ついでこの表面に銀ペーストを用いて対極リードを取り出し、エポキシ樹脂により外装しコンデンサを完成させた。得られたコンデンサは120Hzにおいて、静電容量は $1.2\mu\text{F}/\text{cm}^2$ であり、損失角の正接( $\tan\delta$ )は1.0%であった。尚このタンタル焼結体の液中容量は $1.0\mu\text{F}$ であるので容量達成率は120%であった。

#### (発明の効果)

先きに述べたように固体電解コンデンサの固体電解質に有機半導体であるTCNQ錯体を用いると電気特性とくに高周波特性の優れたコンデンサが得られることがすでに知られているが、その熱安定性および溶解性が悪いため製造上大きな問題となっている。また電気絶縁体である誘電体酸化皮膜上に直接電解重合によって得られる強靱な導電性高分子膜を重合することは不可能であったが本発明により可能となり、有機半導体を固体電解

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質として用いた温度特性、電気特性の優れた固体電解コンデンサを提供することができた。

#### 4. 図面の簡単な説明

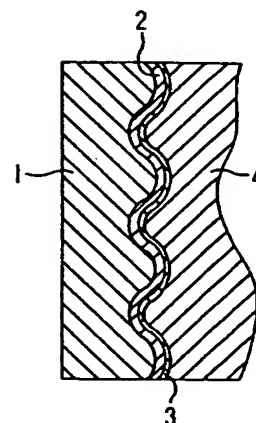
第1図は本発明の固体電解コンデンサの構成を示す概略断面図である。

- 1・・皮膜形成金属
- 2・・誘電体酸化皮膜
- 3・・化学酸化重合により形成した導電性高分子膜
- 4・・電解重合により得られた導電性高分子膜

特許出願人 日本カーリット株式会社

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第1図



# United States Patent [19]

Fukuda et al.

[11] Patent Number: 4,780,796

[45] Date of Patent: Oct. 25, 1988

[54] **SOLID ELECTROLYTIC CAPACITOR**

[75] Inventors: Minoru Fukuda, Maebashi; Hideo Yamamoto, Shibukawa; Isao Isa, Misatomachi, all of Japan

[73] Assignee: The Japan Carlit Co., Ltd., Tokyo, Japan

[21] Appl. No.: 138,591

[22] Filed: Dec. 28, 1987

[30] **Foreign Application Priority Data**

Jan. 13, 1987 [JP] Japan ..... 61-4053  
Feb. 12, 1987 [JP] Japan ..... 61-28497

[51] Int. Cl.<sup>4</sup> ..... H01G 9/00

[52] U.S. Cl. .... 361/433; 29/570.1

[58] Field of Search ..... 29/570.1; 361/433;  
437/1; 429/212, 213

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*Primary Examiner*—Donald A. Griffin

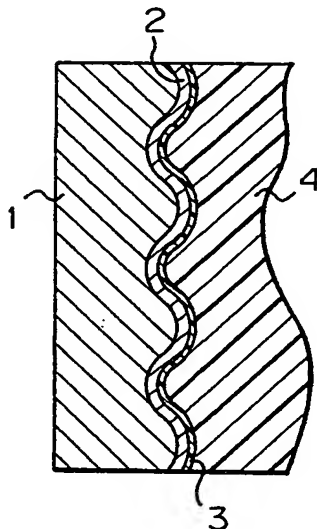
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[57]

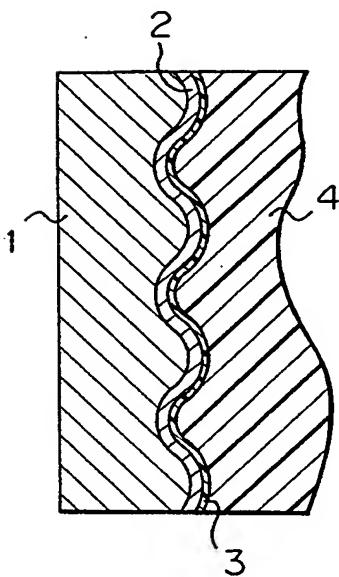
**ABSTRACT**

A solid electrolytic capacitor having excellent characteristics in terms of both electrical properties and thermal stability is obtained by employing a solid electrolyte comprising both an electrically conductive polymer layer (I) formed by a chemical oxidation method and an electrically conductive polymer layer (II) formed by an electrochemical oxidation method.

**5 Claims, 1 Drawing Sheet**



*Fig. 1*



## SOLID ELECTROLYTIC CAPACITOR

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to a solid electrolytic capacitor that utilizes an electrically conductive polymer as a solid electrolyte.

#### 2. Description of the Related Art

The development of digital devices in recent years has given rise to a demand for large-capacity capacitors which have excellent high-frequency characteristics; and studies have been made directed to the application of an electrically conductive polymer in this field.

Examples of known capacitors which have excellent high-frequency characteristics include thin-film, mica and ceramic capacitors. These conventional capacitors, however, involve the problem that, when they are designed to obtain an electrostatic capacity of 1  $\mu\text{F}$  or more, their size is increased, and the production cost is also raised considerably.

Electrolytic capacitors which are known to be large-capacity capacitors include two types, that is, the liquid electrolyte type in which a liquid electrolyte is impregnated, and the solid electrolyte type in which manganese dioxide is employed as a solid electrolyte. The former type of electrolytic capacitor which employs an electrolyte in a liquid state utilizes ion conduction, and there is therefore a remarkably increased resistance in the high-frequency region, whereby the impedance of the capacitor increases disadvantageously. The latter type of electrolytic capacitor employs as a solid electrolyte manganese dioxide and a charge transfer complex consisting of a combination of 7,7,8,8-tetracyanoquinodimethane (hereinafter referred to as TCNQ) and an electron donor.

The type of electrolytic capacitor which employs manganese dioxide as a solid electrolyte is obtained by thermally decomposing manganese nitrate since manganese dioxide is an insoluble solid substance. This type of electrolytic capacitor also has relatively high impedance in the high-frequency region, partly because manganese dioxide has a relatively high specific resistance, and partly because it is subjected to thermal decomposition several times to obtain manganese dioxide. Also a dielectric oxide coating provided on this type of electrolytic capacitor may be readily damaged, and the loss current of the capacitor thus increases to a remarkable extent.

The type of electrolytic capacitor which employs as a solid electrolyte a charge transfer complex consisting of a combination of TCNQ and an electron donor has already been proposed (see Japanese patent public disclosure No. 191414/1983, No. 17609/1983). However, this TCNQ charge transfer complex which has high electrical conductivity suffers from thermal stability and therefor involves a risk of the complex being decomposed during the capacitor manufacturing process to become an insulator.

A type of electrolytic capacitor which employs as a solid electrolyte a heterocyclic polymer obtained by an electrochemical polymerization method has been proposed in recent years (see Japanese patent public disclosure No. 244017/1985, No. 2315/1986).

The electrolytic capacitor described above comprises an electrode having a dielectric oxide coating thereon and a solid electrolyte consisting of an electrically conductive heterocyclic polymer which is formed by an

electrochemical oxidation method. However, forming the electrically conductive heterocyclic polymer on the dielectric oxide coating is impossible or, at least, difficult because the dielectric oxide coating is an insulator.

### SUMMARY OF THE INVENTION

Usually, an electrically conductive polymer is formed by a chemical oxidation method or an electrochemical oxidation method. The polymer which is obtained by the former method has poor mechanical strength. No polymer is formed on the dielectric oxide coating using the latter method because the dielectric oxide coating is an insulator.

It is a first object of the present invention to provide an electrolytic capacitor by employing an electrically conductive polymer as a solid electrolyte for the capacitor.

It is a second object of the present invention to provide an electrolytic capacitor which is excellent in both electrical characteristics and thermal stability superior to that of the conventional capacitors.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description and disclosure.

### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic, partial, sectional view illustrating the construction of a solid electrolytic capacitor according to one embodiment of the present invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present inventors made exhaustive studies with a view to attaining the above objects and have found that the above-described disadvantages of the prior art can be overcome by providing a solid electrolytic capacitor comprising, in combination, an electrode having an adherent dielectric oxide coating thereon and a solid electrolyte comprising both an electrically conductive polymer layer (I) which is formed by a chemical oxidation method, contacting a monomer with an oxidizing agent, and an electrically conductive polymer layer (II) which is formed by electrochemical oxidation method.

The invention will be better understood from the following description taken in conjunction with the accompanying drawing, FIG. 1, which partially shows the construction of an electrical capacitor which embodies the present invention.

The surface of an electrode 1 which is roughened by an electrochemical treatment is oxidized by an electrochemical oxidation treatment or an air oxidation treatment whereby a dielectric oxide coating 2 is formed on the electrode.

A solution containing an oxidizing agent in a concentration of 0.001 mol/l to 2 mol/l is dispersed uniformly on the dielectric oxide coating by dipping, coating or spraying and the oxidizing agent is then brought into contact with a monomer of an electrically conductive polymer (I) or a solution of the monomer in a concentration of more than 0.01 mol/l. Consequently, an electrically conductive polymer layer 3 which is obtained by a chemical oxidation method is formed on the dielectric oxide coating 2. The electrically conductive polymer layer 3 is able to be formed by an inverse procedure in which the monomer is brought into contact with the oxidizing agent.



The electrically conductive polymer layer 3 is used as an anode for electro polymerization. An electrically conductive polymer layer 4 which is obtained by an electrochemical oxidation method is formed in a cell containing a solution of a monomer of an electrically conductive polymer (II) in a concentration of 0.01 mol/l to 5 mol/l and an electrolyte salt in a concentration of 0.01 mol/l to 2 mol/l. Consequently, the electrically conductive polymer layer 4 is formed on the electrically conductive polymer layer 3.

A counter electrode is brought into contact with the electrically conductive polymer layer 4 using an electrically conductive adhesive (silver paste etc.) The capacitor of the present invention is completed by the procedure described above and is then molded with epoxy resin.

The electrode used in the capacitor of this invention is generally selected from either aluminum or tantalum.

Commonly used oxidizing agents include a halogen such as iodine, bromine and bromine iodide; a halide such as antimony pentafluoride, arsenic pentafluoride, silicon tetrafluoride, phosphorus pentachloride, phosphorus pentafluoride, ferri-chloride, aluminum chloride and molybdenum chloride; a protonic acid such as sulfuric acid, nitric acid, fluorosulfuric acid, trifluoromethane sulfuric acid and chlorosulfuric acid; a compound containing oxygen such as sulfur trioxide, nitrogen dioxide and chlorine dioxide; a persulfate such as sodium persulfate, potassium persulfate and ammonium persulfate; and a peroxide such as hydrogen peroxide, peracetic acid and difluorosulfonil peroxide.

The preferred compounds of said oxidizing agent are chlorine dioxide and ammonium persulfate.

Said electrically conductive polymer layer (I) which is formed by a chemical oxidation method is generally selected from the group consisting of polypyrrole, polythiophene, polyaniline and polyfuran. The preferred polymer of said electrically conductive polymer layer (I) is polypyrrole or polyaniline.

Said electrolyte salt consists of an anion and a cation. Commonly used anions include an halogenated anion such as hexafluorophosphate, hexafluoroarsenate, tetrafluoroborate and perchlorate; a halide such as chloride, bromide and iodide; and a sulfonate such as alkylbenzenesulfonate, aminobenzenesulfonate, benzenesulfonate and  $\beta$ -naphthalenesulfonate. The most preferred anion is sulfonate.

Commonly used cations include an alkali metal cation such as lithium, sodium and potassium; and an ammonium cation such as ammonium and tetraalkylammonium.

Suitable electrolyte salts include lithium hexafluorophosphate, lithium hexafluoroarsenate, lithium perchlorate, sodium iodide, sodium hexafluorophosphate, sodium perchlorate, potassium iodide, potassium hexafluorophosphate, potassium hexafluoroarsenate, potassium perchlorate, lithium tetrafluoroborate and tetrabutylammonium toluenesulfonate.

Said electrically conductive polymer layer (II) which is formed by an electrochemical oxidation method is generally selected from the group consisting of polypyrrole, polythiophene, polyaniline and polyfuran. The most preferred electrically conductive polymer layer (II) is polypyrrole or polyaniline.

It is known that an electric capacitor having a TCNQ charge transfer complex as an electrolyte has excellent high-frequency characteristics. However, the TCNQ charge transfer complex suffers from thermal stability

and therefore involves a risk of the complex being decomposed during the capacitor manufacturing process to become an insulator. Furthermore, forming an electrically conductive heterocyclic polymer having excellent mechanical strength by an electrochemical oxidation method on an electrode having a dielectric oxide coating is impossible, because the dielectric oxide coating is an insulator.

The above-described disadvantages can be overcome by the solid electrolytic capacitor of the present invention. This solid electrolytic capacitor having an organic semiconductor as a solid electrolyte is excellent in both electrical characteristics and thermal stability.

The present invention will be explained more specifically below by way of Examples, though it is in no way restricted to these Examples.

#### EXAMPLE 1

An aluminium anode foil (thickness: 60  $\mu$ m) having a dielectric aluminium oxide coating formed thereon by an electrochemical oxidation treatment was dipped in an aqueous solution containing 0.04 mol/l ammonium persulfate under reduced pressure conditions for 10 minutes and then dried.

The anode foil was dipped in acetonitrile containing 2.0 mol/l pyrrole monomer under reduced pressure conditions for 10 minutes. A thin layer of polypyrrole was formed on the dielectric aluminium oxide coating by a chemical oxidation method.

Subsequently, the anode foil was dipped in an aqueous solution containing 0.2 mol/l pyrrole monomer, 0.02 mol/l oxalic acid and 0.05 mol/l tetrabutylammonium toluene-sulfonate as an electrolyte. The anode foil was used as an anode and a stainless steel plate was used as a cathode. A uniform black layer of polypyrrole was formed galvanostatically on the anode foil under a current density of 0.5 mA/cm<sup>2</sup> applied for 150 minutes. After a counter electrode had been brought into contact with the black layer of polypyrrole using a silver paste, a capacitor was obtained and then molded with epoxy resin.

The characteristics of the obtained capacitor are shown in Table 1.

#### EXAMPLE 2

Ethyl ether containing 0.1 mol/l iodine was sprayed on an aluminium anode foil (thickness: 60  $\mu$ m) having a dielectric aluminium oxide coating formed thereon by an electrochemical oxidation treatment and the anode foil was then dried.

After dipping the anode foil in pyrrole monomer for 30 minutes under reduced pressure conditions, a black layer of polypyrrole was formed on the dielectric aluminium oxide coating by a chemical oxidation method. The following procedures were carried out in a similar manner to Example 1.

The characteristics of the obtained capacitor are shown in Table 1.

#### EXAMPLE 3

An aluminium anode foil (thickness: 60  $\mu$ m) having a dielectric aluminium oxide coating thereon was dipped in an aqueous solution containing 0.02 mol/l ferri chloride for 2 minutes under reduced pressure conditions and then dried.

After dipping the anode foil for 30 minutes in an aqueous solution containing 0.1 mol/l pyrrole monomer, a black layer of polypyrrole was formed on the

dielectric aluminium oxide coating by a chemical oxidation method. The following procedures were carried out in a similar manner to Example 1.

The characteristics of the obtained capacitor are shown in Table 1.

#### EXAMPLE 4

An aluminium anode foil (thickness: 60  $\mu\text{m}$ ) having a dielectric aluminium oxide coating formed thereon by an electrochemical oxidation method was dipped in pyrrole monomer. When a gaseous mixture containing 5 vol% chlorine dioxide was brought into contact with the anode foil for 5 minutes, a black layer of polypyrrole was formed on the dielectric aluminium oxide coating by a chemical oxidation method. The following procedures were carried out in a similar manner to Example 1.

The characteristics of the obtained capacitor are shown in Table 1.

#### COMPARATIVE EXAMPLE 1

An electrochemical oxidation treatment was carried out similar to Example 1 except that a layer of polypyrrole was formed on a dielectric aluminium oxide coating by a chemical oxidation method. Polypyrrole was formed on only a part of the dielectric aluminium oxide coating and no uniform layer of polypyrrole was formed.

#### EXAMPLE 5

An aluminium anode foil (thickness: 60  $\mu\text{m}$ ) having a dielectric aluminium oxide coating formed thereon by an electrochemical oxidation treatment was dipped in aniline monomer.

After a gaseous mixture containing 5 vol% chlorine dioxide had been brought into contact with the anode foil for 10 minutes, a layer of polyaniline was formed on the dielectric aluminium oxide coating by a chemical oxidation method.

Subsequently, the anode foil was dipped in an aqueous solution containing 1.0 mol/l aniline monomer and 1.0 mol/l sulfuric acid as an electrolyte. The anode foil was used as an anode and a platinum plate as a cathode. A uniform dark green layer of polyaniline was formed on the anode foil galvanostatically under a current density of 0.5 mA/cm<sup>2</sup> applied for 150 minutes. After a counter electrode was brought into contact with the dark green layer of polyaniline using a silver paste, a capacitor was obtained and then molded with epoxy resin.

The characteristics of the obtained capacitor are shown in Table 1.

#### EXAMPLE 6

A sintered tantalum anode pellet having a dielectric tantalum oxide coating formed thereon by an electrochemical oxidation treatment was dipped in an aqueous solution containing 0.04 mol/l ammonium persulfate under reduced pressure conditions for 5 minutes and then dried.

The anode pellet was dipped in an aqueous solution containing 2.0 mol/l pyrrole monomer and 0.02 mol/l adipic acid under reduced pressure conditions for 10 minutes. A thin layer of polypyrrole was formed on the dielectric tantalum oxide by a chemical oxidation method.

Subsequently, the anode pellet was dipped in an aqueous solution containing 0.2 mol/l pyrrole monomer,

0.02 mol/l oxalic acid and 0.05 mol/l lithium perchlorate as an electrolyte.

The anode pellet was used as an anode and a stainless steel plate as a cathode. A uniform black layer of polypyrrole was formed galvanostatically on the anode pellet under a current density of 0.5 mA/cm<sup>2</sup> applied for 150 minutes. After a counter electrode had been brought into contact with the black layer of polypyrrole using silver paste, a capacitor was obtained and then molded with epoxy resin.

The characteristics of the obtained capacitor are shown in Table 1.

#### EXAMPLE 7

A sintered tantalum anode pellet having a dielectric tantalum oxide coating formed thereon by an electrochemical oxidation treatment was dipped in pyrrole monomer.

After bringing a gaseous mixture containing 5 vol% chlorine dioxide into contact with the anode pellet for 5 minutes, a black layer of polypyrrole was formed on the dielectric tantalum oxide by a chemical oxidation method.

The following procedures were carried out in a similar manner to Example 6.

The characteristics of the obtained capacitor are shown in Table 1.

TABLE 1

Ex.	Anode	Solid Electrolyte	Electrical Characteristics	
			Cap ( $\mu\text{F}/\text{cm}^2$ )	$\tan \delta$ (%)
1	aluminium	polypyrrole	2.2	1.5
2	aluminium	polypyrrole	2.0	1.3
3	aluminium	polypyrrole	2.1	1.8
4	aluminium	polypyrrole	2.2	1.3
5	aluminium	polyaniline	2.0	1.2
6	tantalum	polypyrrole	1.2	1.0
7	tantalum	polypyrrole	1.2	0.9

In Table 1, Cap means electrostatic capacity at 120 Hz,  $\tan \delta$  means dielectric loss tangent at 120 Hz. Electrostatic capacity of the aluminium anode foil and the tantalum pellet used in Example show 2.0  $\mu\text{F}/\text{cm}^2$  and 1.0  $\mu\text{F}$ , respectively, when an aqueous solution containing 50 g/l boric acid, 50 g/l citric acid and 50 ml/l ammonia water (28 wt%) is employed as liquid electrolyte.

What is claimed is:

1. A solid electrolytic capacitor having excellent characteristics in terms of both electrical properties and thermal stability comprising, in combination, an electrode having an adherent dielectric oxide coating thereon and a solid electrolyte comprising an electrically conductive polymer layer (I) formed by a chemical oxidation method comprising contacting a monomer with an oxidizing agent and an electrically conductive polymer layer (II) formed on the electrically conductive polymer layer (I) by an electrochemical oxidation method.

2. The solid electrolytic capacitor according to claim 1, wherein said electrode is made of aluminum or tantalum.

3. The solid electrolytic capacitor according to claim 1, wherein said electrically conductive polymer layer (I) is polypyrrole or polyaniline.

4. The solid electrolytic capacitor according to claim 1, wherein said oxidizing agent is chlorine dioxide.

5. The solid electrolytic capacitor according to claim 1, wherein said electrically conductive polymer layer (II) is polypyrrole or polyaniline.

\* \* \* \* \*

**UNITED STATES PATENT AND TRADEMARK OFFICE**  
**CERTIFICATE OF CORRECTION**

**PATENT NO. :** 4,780,796

**DATED :** October 25, 1988

**INVENTOR(S) :** FUKUDA et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Title Page, [30] Foreign Application Priority Data:**

Replace "61-4053" with --62-4053--

Replace "61-28197" with --62-28197--.

Signed and Sealed this  
Fourteenth Day of September, 1993



Attest:

**BRUCE LEHMAN**

*Attesting Officer*

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